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CHNO ENERGETIC POLYMER SPECIFIC HEAT PREDICTION FROM THE PROPOSED NOMINAL/GENERIC (N/G) C_P CONCEPT

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13. ABSTRACT ***(Maximum 200 Words)***

The importance of the specific heat (C_P) of CHNO energetic polymers relative to their impact shock sensitivity has been documented in MICOM TR-RD-SS-95-2, AMCOM TR-RD-SS-99-8, and RDECOM TR-AMR-SS-06-09. A follow-on-report, RDECOM TR-AMR-SS-06-35, documents a proposed nominal/generic (N/G) C_P for CHNO energetic materials. The motivation for this proposed N/G C_P was it's utilization to predict C_P for energetic polymers whose C_P was unknown. This report documents the successful application of the N/G C_P concept to predict the C_P for a relatively new CHNO explosive, FOX-7.

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I. INTRODUCTION

References 1 through 6 have demonstrated that the one-dimensional (1-D) plane impact shock sensitivity of several important energetic polymeric chemical CHNO compounds can be correlated to how much heat energy, Δ (v.e.)$_{TR}$, they can absorb before some type of reaction (melt, phase transition, deflagration, or detonation) occurs. The amount of internal energy that can be soaked up is directly related to the material's specific heat (C_P) magnitude and variation with temperature (T). See Section II.A. for more details about the Δ (v.e.)$_{TR}$ concept that relates C_P heat absorption to impact shock sensitivity.

The C_P (T) of CHNO energetic polymers is a very important property from both heat and impact shock sensitivity view points. As such, a simple C_P (T) estimation/prediction procedure is also desirable and very important when experimental data may not be available.

One attempt at a C_P (T) estimation/prediction scheme is documented in Reference 7 and briefly described in Section II.B. of this report. This is the so called Nominal/Generic (N/G) C_P per average atom concept.

An N/G C_P was proposed based on the observation that the C_P's per average atom for CHNO explosives at a given temperature did not deviate very much from each other. So in lieu of experimental C_P data for a CHNO explosive compound, the N/G C_P could be utilized to make a C_P prediction.

A successful application of this C_P estimation procedure is documented in Section III of this report for the FOX-7 CHNO explosive compound. This application is called "successful" because the predicted C_P agreed remarkably well with C_P results computed by a much more complex and sophisticated analysis.

II. BACKGROUND INFORMATION

A. The Δ (v.e.)$_{TR}$ Concept

Essentially, the area Δ (v.e.)$_{TR}$ under the C_P versus Temperature (T) plots between temperature limits (Experimental Test Temperature (T_{EXP}) and Reactive Temperature (T_R)) is a measure of how much atomic vibratory energy explosives can absorb before a reaction occurs. The reaction may be melting, phase change, decomposition, burning, or even detonation. Thus, to a good approximation, it could be expected that if $\Delta(v.e)_{TR}$ amount of energy is suddenly added via impact shock loading, then a reaction may occur.

This Δ (v.e.)$_{TR}$ concept, that impact shock sensitivity or shock induced reactivity of energetic materials could be related to their specific heat ($\mathbf{C}_P$) variation with temperature, was demonstrated in References 1 and 2 for RDX, TETRYL, PETN, TNT, and TATB, which are basic secondary reactive compounds.

In References 3 and 4, the Δ (v.e.)$_{TR}$ ideas were demonstrated for HMX and HNS which are also important basic secondary explosive compounds. The impact shock response of these seven compounds ranges from very insensitive to highly sensitive. Most of these seven basic energetic compounds have been the main ingredient of useful explosive mixtures.

One such mixture is the plastic bonded explosive designated as PBX-9502 that is 95 percent TATB and 5 percent KEL-F80. PBX-9502 has been rather extensively tested via 1-D shock loading at various temperatures, and its thermal characteristics have also been experimentally explored. Consequently, with this much information available, Δ (v.e.)$_{TR}$ concept computations were made for PBX-9502. The exploratory comparative results for this important energetic material were highly affirmative and are documented in References 5 and 6.

General details of the exploratory computation and experimental data comparisons involved in a general Δ (v.e.)$_{TR}$ assessment are contained in the following paragraphs.

The thermal atomic vibratory energy increment, Δ (v.e.)$_{TR}$, is related to macroscopic critical particle (or mass) velocities (U_{PCR}) and impact shock pressures via Equations (1) through (6).

For certain explosives, a good estimate of the critical particle velocity, U_{PCR} , where a reaction (or detonation) occurs is:

$$U_{PCR1} = \sqrt{\frac{\Delta(v.e.)_{TR}}{m_{AV}}} \tag{1}$$

In some circumstances, a better estimate of the critical particle velocity is:

$$U_{PCR2} = \sqrt{\frac{2\Delta(v.e.)_{TR}}{m_{AV}}} = \sqrt{2}\ \ U_{PCR1} \tag{2}$$

where:

$$\Delta(\text{v.e.})_{T_R} = \int_{T_{EXP}}^{T_R} C_p dT \qquad (3)$$

= Thermal vibratory energy per atom between T_{EXP} and T_R, Gram $(Cm/Sec)^2$.

C_P = Specific heat per atom as a function of temperature.

m_{AV} = Average mass of an atom in the material, Grams (Appendix A).

T_{EXP} = Temperature at which experimental impact shock tests are conducted. This is normally room temperature (RT≈ 300 ˚K) but can (and should) be done at higher and lower temperatures.

T_R = Temperature at which some thermally induced reaction occurs (decomposition, melting, phase change, detonation, etc.).

U_{PCR2} = Particle velocity, U_P, such that the shock induced internal energy (e_i) is equal to $\Delta(\text{v.e,})_{TR}$.

U_{PCR1} = Particle velocity, UP, such that the total shock induced energy (e_t) (kinetic plus internal) is equal to $\Delta(\text{v.e.})_{TR}$.

e_t = $m_{AV}U^2_P$ = total shock energy per average atom.

e_i = $\frac{m_{AV}}{2}U^2_P = e_k$ = internal or kinetic energy of the shocked material per average atom.

When good comparisons can be made, it has been generally found that experimental detonation particle (mass) velocity threshold values (U_{PTH}) will be somewhere between U_{PCR1} and U_{PCR2} .

Certain explosives, when heated to higher and higher temperatures, melt before they explode (RDX and TNT, for example). This melting will require that the heat of fusion (ΔH_F) be absorbed by the material at $T=T_{MELT}$ conditions before the temperature will increase [9, 10]. Consequently, if T_{EXP} is less than T_{MELT}, then the total heat absorbed from $T = T_{EXP}$ to $T = T_{EXPL} = T_R$ is:

$$\Delta(\text{v.e.})_{T_R} = \int_{T_{EXP}}^{T_{MELT}} C_p dT + \Delta H_F + \int_{T_{MELT}}^{T_{EXPL}} C_p dT. \qquad (4)$$

Therefore, for solid energetic materials which melt prior to explosion, then $\Delta(\text{v.e.})_{TR}$, as defined by Equation (4) is employed in Equations (1) and (2) to compute U_{PCR1} and U_{PCR2}, respectively. Note that melting is just one example of a phase transformation which may require an enthalpy increment (ΔH_T) to be activated. For example, HMX can exist in different solid polymorphic forms. At a certain temperature, T_T, one form may change to another form if the heat energy of transformation (ΔH_T) is supplied. Therefore, ΔH_T should be added to Equations (3) and (4) if T_R is greater than T_T.

Note that Δ (v.e.)$_{TR}$ as defined by Equations (3) and (4) is actually an enthalpy increment (ΔH). However, it was shown via numerical examples in Appendix B of Reference 1 that, under the experimental C_P acquisition conditions, the pressure times volume terms were minute compared to the C_P integral, $\int_{T_{EXP}}^{T_R} C_p dT$. Thus, $\int_{T_{EXP}}^{T_R} C_p dT$ is essentially all of the internal energy difference caused by thermal stimulation during standard tests at atmospheric pressure to determine the specific heat characteristics.

Once Δ (v.e.)$_{TR}$ and U_{PCR} values are computed, the corresponding shock velocity (U_{SCR}) is ascertained from experimental data for U_S as a function of the particle velocity, U_P. The experimental relationship is usually linear and written empirically as:

$$U_S = C_O + S\,U_P \tag{5}$$

When $U_P = U_{PCR}$ and $U_S = U_{SCR}$ are determined, the shock pressure is computed from the following well known relation:

$$P_S = \rho_o\, U_S\, U_P, \tag{6}$$

Where ρ_o = Material density (grams/cm^3).

Then U_{PCR}, U_{SCR}, and P_{SCR} may be compared to experimental shock-induced reaction threshold information to check the validity of the above Δ (v.e.)$_{TR}$ theory to denote reactive conditions under impact shock stimuli. The numerical computations involved in a Δ (v.e.)$_{TR}$ assessment are straightforward and may be performed with a hand-held calculator.

It must be emphasized that any possible effect of pressure on C_P is not taken into account in the present analysis. The basic idea is that if a quantity of thermal vibration energy, Δ (v.e.)$_{TR,}$ under quiescent conditions is able to create a reaction, then the same amount of energy added by an impact shock (e_i or e_t) should also cause some type of reaction. <u>The shock-induced reaction may not be the same type as the temperature induced reaction, but will nevertheless, be a reaction of some kind.</u> It may be less or more severe than the thermally induced reaction.

The C_P unit of calorie/(atom °K) was employed in plots of C_P versus T information, which are shown in this report. This is because the Boltzman constant, k_B=0.33 x 10^{-23} calories/(atom °K) and the maximum C_P at high temperatures for many materials is 3 k_B $\approx$1.0 x 10^{-23} calories/(atom °K). This is a good mnemonic reference level for comparison purposes. It was noted in Reference 1 that the average C_P per atom for most polymers never reaches the 3 k_B level before a reaction (phase change, melting, glass-to-rubber transition, or even detonation) occurs.

Actually, C_P for some atoms, or combinations of atoms, probably reaches the 3 k_B level and causes a reaction at some T_R. But C_P for a large number of atoms remains much less than 2 k_B. Thus, a large amount of the possible thermal vibratory energy is never activated and the average C_P per atom remains relatively low [14]. In many cases, important temperature

induced reactions occur near the average $C_P \approx 2\ k_B$ level at moderate temperatures (400 to 600 °K).

B. The N/G C_P Concept

It was first documented in Reference 1 that the C_P [Cal/(atom °K)] magnitudes (at a given T) for five solid explosive compounds (RDX, TETRYL, PETN, TNT, and TATB) did not differ very much from each other. In Reference 3, it was demonstrated that the C_P for HNS was very close to that for TATB, and the C_P for HMX was somewhat less than the TATB C_P at the higher temperatures. Liquid TNT has a larger C_P (at a given T) than these solid energetic compounds. These statements are corroborated by the experimental C_P information exhibited in Figures 1 through 4 of Reference 7.

So with two exceptions (melted TNT and δ – HMX), the C_P per atom of five important secondary energetic compounds all had very similar magnitudes near that for TATB. HNS also has the same magnitude and trend (non-linear variation) with temperatures as TATB. The other explosives (RDX, TNT, TETRYL and PETN) C_P have a linear variation (a + b T) over most of their temperature range.

The amount of heat energy these compounds and mixtures can absorb varies considerately. TATB and PBX-9502 can soak up more heat energy, $\Delta\ (\text{v.e.})_{TR}$, than the others by a considerable margin. That is, their reactive temperatures, T_R, were much greater than the other compounds (more than 100 °K for TNT, HNS and HMX and over 200 °K for TETRYL, PETN, and RDX).

So based on the above remarks and similar remarks in References 1, 3, and 5, a nominal C_P per average atom was proposed and defined as shown in Figure 2 and listed in Table 1. These nominal C_P magnitudes at Room Temperature (RT) and above are very similar to those of TATB, particularly at the high temperatures. Below RT, the proposed N/G C_P magnitudes are very close to (or equal to) the RDX C_P values and TNT C_P values near absolute zero.

In Reference 7, two examples (TNT and HMX) were selected for comparative computations where U_{PCR} and P_{SCR} were calculated via the experimental C_P and the N/G C_P. TNT has a high C_P relative to the N/G C_P and HMX has a low C_P relative to the N/G C_P. Two cases were considered for TNT where the large liquid C_P was included in Case 1.

Consequently, excluding Case 1 for TNT where the large liquid C_P had to be included in the U_{PCR} (EXP) and P_{SCR} (EXP) computations, then for TNT (Case 2), PBX-9502, and HMX, the maximum percentage differences between the (EXP) C_P and (N/G) C_P results were bounded by:

$$\frac{\Delta U_{PCR}}{U_{PCR}(EXP)} = \frac{U_{PCR}(N/G) - U_{PCR}(EXP)}{U_{PCR}(EXP)}\ X\ 100.0 < |\ 2.5\%\ | \qquad (9)$$

$$\frac{\Delta P_{SCR}}{P_{SCR}(EXP)} = \frac{P_{SCR}(N/G) - P_{SCR}(EXP)}{P_{SCR}(EXP)}\ X\ 100.0 < |\ 3.5\%\ | \qquad (10)$$

These small differences provide considerable credibility for the proposed N/G C_P per average atom concept for most CHNO energetic materials.

III. EXAMPLE OF C_P PREDICTION FOR FOX-7 VIA THE N/G CONCEPT

The relatively new CHNO explosive compound, FOX-7 (1, 1-Diamino-2, 2-Dinitroethylene), has generated a considerable amount of interest among explosive investigators within the last decade. References 8 through 11 are a good sampling of the experimental and theoretical efforts devoted to this energetic material.

However, there has been no experimental determination of FOX-7's specific heat, but there is a rather sophisticated and complex theoretical prediction of C_P as a function of T given in Reference 8. As such, this fits our search criteria for a good CHNO energetic compound to apply the N/G C_P concept for predicting the C_P magnitudes.

Thus, FOX-7 is a good choice for a C_P prediction example Via the N/G C_P concept because:

1. No experimental C_P (T) data for FOX -7 were available and, consequently, could not have influenced the proposed N/G C_P magnitudes.

2. There was, however, a theoretical computation of C_P (T) for FOX-7 that was available for comparison with C_P (T) from any other predictive scheme or with experimental data.

In Appendix A, the Molecular Weight (MW) and m_{AV} (mass of an <u>average</u> atom) for FOX-7 are computed. These values are:

$MW = 148.086$ grams/mole

$m_{AV} = 1.756239\ (10^{-23})$ grams/atom

Also for $C_2 H_4 N_4 O_4 = C_i H_j N_k O_l$

$q = i + j + k + l = 14.0$ atoms/molecule

From various sources, Avogadro's number is:

$N_{AV} = 6.02252\ (10^{+23}) =$ molecules/MW

= Number of molecules per mole (MW) in a chemical compound. Also N_{AV} is the number of atoms in an Atomic Weight (AW) of an element.

As shown in Appendix A, the number of atoms per mole (MW) of FOX-7 can be computed by two different ways. These are:

$$1.\quad NAPMW_1 = \frac{MW}{m_{AV}} = \frac{Grams/MW}{Grams/Atom} = \frac{148.086}{1.756329(10^{-23})}$$

$$= 84.315638\ (10^{+23})\ Atoms/MW$$

$$2.\quad NAPMW_2 = q\ N_{AV} = \frac{Atoms}{Molecule} \bullet \frac{Molecules}{MW}$$

$$= (14.0)\ (6.02252 \times 10^{+23})$$

$$= 84.315280\ (10^{+23})\ \frac{Atoms}{MW}$$

These results for NAPMW agree to three decimal places and so

$$NAPMW = 84.315\ (10^{+23})\ Atoms/MW$$

is used in the following computations to predict the FOX-7 C_P from the N/G C_P. That is, for a given temperature (T):

$$FOX\text{-}7\ C_P = (NAPMW)\ C_{PN/G}$$

$$= \left(\frac{Atom}{MW}\right)\left(\frac{Cal.}{Atom - °K}\right) = \left(\frac{Cal.}{MW - °K}\right)$$

Also:

$$FOX\text{-}7\ C_P = 4.184\ C_P \left(\frac{Cal.}{MW - °K}\right) = \left(\frac{Joules}{MW - °K}\right)$$

These C_P prediction computations are listed in Table 2 for a wide range of temperatures (100 to 650 °K). The results, C_P [Joules/ (MW-°K)], are plotted versus T (°K) in Figure 1.

Table 3 lists the FOX-7 theoretical C_P [Joules/ (MW-°K)] results from Reference 8, (Fig. 6). This information is also plotted in Figure 1 for comparative purposes. The C_P magnitudes from these two predictive schemes are in remarkably close agreement.

Table 3 also contains the conversion of the Reference 8 FOX-7 C_P in [Cal/ (Atom-°K)]. These results are plotted in Figure 2 along with the proposed N/G C_P that is in the same units. As expected from the Figure 1 comparison, the FOX-7 C_P and the N/G C_P, on a per average atom basis, agree exceptionally well.

IV. DISCUSSION

As shown in Figure 1, the FOX-7 C_P (T) magnitudes, predicted from the proposed N/G C_P concept in the present report and the theoretical C_P results in Reference 8, compare exceptionally well. Table 4 lists the magnitude and the percentage differences. The percentage difference is within 6.0 percent for 100 °K $\leq T \leq$ 400 °K.

The largest negative difference (-5.9 percent) occurs at 100 °K and the greatest positive difference (+3.9 percent) occurs at 400 °K. So the predictive trends (or slopes) with temperature are slightly different but the C_P magnitudes are quite comparable. This is remarkable, considering the differences in sophistication and complexity between the predictive methods.

V. RECOMMENDATIONS

As a result of the present analysis and comparison of predicted C_P (T) results for the FOX-7 CHNO explosive compound, the following recommendations are made:

1. Experimental C_P data for FOX-7 should be acquired:
   a. To compare with both C_P predictions.
   b. To have the authoritative C_P for use in the Δ $(v.e.)_{TR}$ concept impact shock sensitivity computations.
2. The temperature range should be from 100 °K to a practical upper limit from experimental considerations. See Reference 11 for documentation of early work on thermal sensitivity.
3. Plane shock impact experiments should be performed to ascertain a lower threshold detonation limit for U_P or P_S. This should be done for more than one temperature (T_{EXP}). Reference 5 documents a Δ $(v.e.)_{TR}$ concept shock sensitivity analysis for PBX-9502 at four T_{EXP} temperatures (218, 300, 348 and 525 °K).
4. Predict the FOX-7 C_P (T) variation using Satoh's scheme for submolar group additive contributions to the total C_P of a polymer compound. See References 12 and 13 for further information on this additive property as applied to inert polymers.

With regard to recommendations 1, 2 and 3, this experimental data may be available for FOX-7, but if so, it is not known to the author of this report.

With regard to recommendation No. 4, some rather affirmative preliminary C_P predictions via the Satoh submolar group additive property have been made for TNT and RDX. Similar computations will be made for FOX-7 and all these C_P predictive results for energetic polymer compounds will be published in a forthcoming report.

The above recommendations/applications/comments concerning explosives in this report should also be valid for solid CHNO rocket propellants.

Table 1. The Generic C_P per Average Atom for CHNO Explosives

T	T	C_P	Remarks
°K	°C	$\frac{\text{Cal}}{\text{Atom - °K}}$	~
0.0	-273	0.0000	↑
7.0	-266	$0.001344(10^{-23})$	Same as
15.0	-258	$0.01463(10^{-23})$	RDX (S.C.)***
78.0	-195	$0.1629(10^{-23})$	↓
100.0	-173	$0.2000(10^{-23})$	↑
150.0	-123	$0.2611(10^{-23})$	|
200.0	-73	$0.3222(10^{-23})$	|
218.0	-55	$0.3442(10^{-23})$	|
250.0	-23	$0.3833(10^{-23})$	See Note 1
293.0	20	$0.4359(10^{-23})$	|
300.0	27	$0.4444(10^{-23})$	|
348.0	75	$0.5031(10^{-23})$	|
350.0	77	$0.5056(10^{-23})$	|
400.0	127	$0.5667(10^{-23})$	|
450.0	177	$0.6277(10^{-23})$	|
500.0	227	$0.6889(10^{-23})$	|
525.0	252	$0.7194(10^{-23})$	|
550.0	277	$0.7500(10^{-23})$	↓
600.0	327	$0.7600(10^{-23})$	↑
650.0	377	$0.7600(10^{-23})$	Same as
669.0	396	$0.7600(10^{-23})$	TATB
700.0	427	$0.7600(10^{-23})$	↓

***S.C. = Single Crystal

Note 1: C_P [Cal/(Atom - °K) $= [0.2000 + 0.001222\ (T - 100)]\ 10^{-23}$

$= [0.07780 + 0.001222\ T\ (°K)]\ 10^{-23}$

For: $100 \leq T\ (°K) \leq 550$

Table 2. FOX-7 C_P Prediction Via the Proposed N/G C_P

T	T	C_P (N/G)	NAPMW	C_P FOX-7	C_P FOX-7	C_P FOX-7
°K	°C	$\frac{\text{Cal.}}{\text{Atom} - °K}$	$\frac{\text{Atoms}}{\text{MW}}$	$\frac{\text{Cal.}}{\text{MW} - °K}$	$\frac{\text{Joules}}{\text{MW} - °K}$	$\frac{\text{Joules}}{\text{Gram} - °K}$
0	-273	0.0	$84.315\ (10^{+23})$	0.0	0.0	0.000
100	-173	$0.2000\ (10^{-23})$	$84.315\ (10^{+23})$	16.863	70.555	0.476
150	-123	$0.2611\ (10^{-23})$	$84.315\ (10^{+23})$	22.015	92.109	0.622
200	-73	$0.3222\ (10^{-23})$	$84.315\ (10^{+23})$	27.166	113.664	0.768
250	-23	$0.3833\ (10^{-23})$	$84.315\ (10^{+23})$	32.318	135.218	0.913
300	27	$0.4444\ (10^{-23})$	$84.315\ (10^{+23})$	37.470	156.773	1.059
350	77	$0.5056\ (10^{-23})$	$84.315\ (10^{+23})$	42.630	178.363	1.204
400	127	$0.5667\ (10^{-23})$	$84.315\ (10^{+23})$	47.781	199.917	1.350
450	177	$0.6277\ (10^{-23})$	$84.315\ (10^{+23})$	52.925	221.436	1.495
500	227	$0.6889\ (10^{-23})$	$84.315\ (10^{+23})$	58.085	243.026	1.641
550	277	$0.7500\ (10^{-23})$	$84.315\ (10^{+23})$	63.236	264.580	1.787
600	323	$0.7600\ (10^{-23})$	$84.315\ (10^{+23})$	64.079	268.108	1.810
650	377	$0.7600\ (10^{-23})$	$84.315\ (10^{+23})$	64.079	268.108	1.810

MW (FOX-7) = 148.086 Grams/Mole

Table 3. FOX-7 Computed Specific Heat Results for FOX-7 From Reference 8, (Fig. 6)

T	T	C_P* (Fig.6)	C_P	C_P	C_P**
°K	°C	$\frac{\text{Joules}}{\text{Cell Mole} - °K}$	$\frac{\text{Joules}}{\text{Mole} - °K}$	$\frac{\text{Cal.}}{\text{Mole} - °K}$	$\frac{\text{Cal.}}{\text{Atom} - °K}$
0	-273	0.00	0.00	0.0000	0.0000 (10^{-23})
50	-223	180.00	45.00	10.7553	0.1276 (10^{-23})
100	-173	300.00	75.00	17.9254	0.2126 (10^{-23})
150	-123	380.00	95.00	22.7055	0.2693 (10^{-23})
200	-73	475.00	118.75	28.3819	0.3366 (10^{-23})
250	-23	550.00	137.50	32.8633	0.3898 (10^{-23})
300 (RT)	27	640.00	160.00	38.2409	0.4535 (10^{-23})
350	77	705.00	176.25	42.1248	0.4996 (10^{-23})
400 (EOD)	127	770.00	192.50	46.0086	0.5457 (10^{-23})

* The C_P from Fig. 6 of Reference [8] is for 4 moles of FOX-7.

FOX-7 $\rightarrow C_2 H_4 N_4 O_4 \rightarrow$ q = 14.0 Atoms/Molecules

N_{AV} = Avogadro's number = 6.02252 (10^{+23}) = Molecules/Mole

NAPMW = q N_{AV} = 84.315 (10^{+23}) = Atoms/Mole

** C_P [Cal/ (Atom - °K)] = C_P [Cal/ (Mole - °K)] / (NAPMW)

RT = Room Temperature

EOD = End of Data

Table 4. FOX-7 C_P (T) Prediction Comparison

T	T	C_{P_1}	C_{P_2}	ΔC_P	$\frac{\Delta C_P}{C_{P_1}}(100)$
°K	°C	$\frac{\text{Joules}}{\text{Mole} - °K}$	$\frac{\text{Joules}}{\text{Mole} - °K}$	$\frac{\text{Joules}}{\text{Mole} - °K}$	Percentage Difference
		Ref. [8], (Table 3)	Present Report (Table 2)	C_{P_2} - C_{P_1}	%
0	.273	0.000	0.000	0.000	0.00
100	-173	75.000	70.555	-4.445	-5.93
150	-123	95.000	92.109	-2.891	-3.04
200	-73	118.750	113.664	-5.086	-4.28
250	-23	137.500	135.218	-2.282	-1.66
300 (RT)	27	160.00	156.773	-3.227	-2.02
350	77	176.250	178.363	+2.113	+1.20
400 (EOD)	127	192.500	199.917	+7.417	+3.85

$$\frac{\Delta C_P}{C_{P_1}}(100) = \left(\frac{C_{P_2} - C_{P_1}}{C_{P_1}}\right) \text{ x } 100.00 = \text{Percent Difference}$$

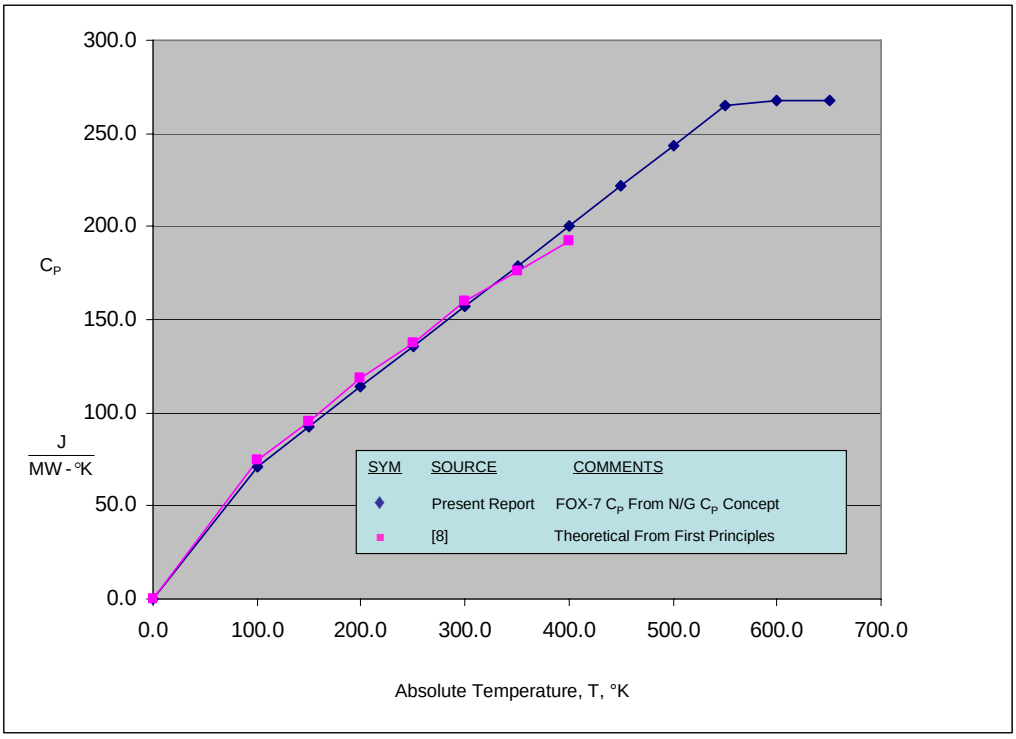

Figure 1. FOX-7 C_P Prediction Comparison

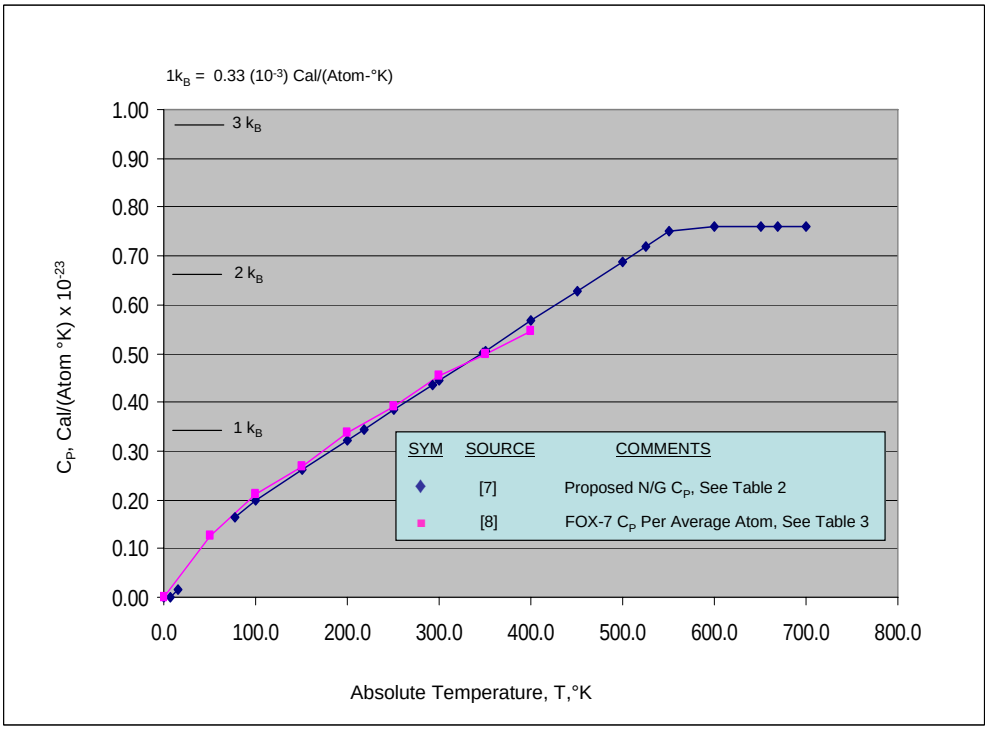

Figure 2. Comparison of the Proposed N/C C_P and the Calculated C_P for FOX-7 From Reference 8

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APPENDIX A
COMPUTATION OF m_{AV}, d_{1av} and MW for FOX-7

APPENDIX A

Computation of m_{AV}, d_{1av} and MW for FOX-7

The solid materials considered in this study were chemical mixtures. For these mixtures, the weighted average mass, m_{AV}, of a single atom in the material was desired.

First, it was necessary to compute the mass of a single atom for each of the elements contained in the solid. The solid was composed of one or more of the following elements:

Carbon, C; Hydrogen, H; Nitrogen, N; Oxygen, O:

The mass of a single atom of these elements is:

$$m = \frac{AW}{N_{AV}} = \frac{\text{gram/(gram - mole)}}{\text{atoms/(gram - mole)}} = \frac{\text{grams}}{\text{atom}} \qquad \text{[A-1]}$$

Where:

$$AW = \frac{\text{grams}}{\text{gram - mole}}$$

$$\text{Nav = Avagadros Number} = 6.02252 \times 10^{+23} \ \frac{\text{atoms}}{\text{gram - mole}}$$

Table A-1 lists AW and m for each of the elements in the above list. Values of Nav and AW are from various chemistry text books and handbooks.

To compute the average weight (m_{AV}) of an atom in the material, the chemical formula or proportional chemical composition is required. Of course, the weight (m) of each elemental atom must be known, since m_{AV} is just a weighted average of the elemental atoms in the material. The procedure is valid for mixtures of compounds as well as compounds. See References [1 & 3] for examples.

When m_{AV} is computed, then the average space between the atoms (d_{1AV}) is given by the following relation:

$$d_{1av} = \left(\frac{m_{AV}}{\rho_\circ} \right)^{1/3} = \text{cm} \qquad \text{[A-2]}$$

Computations of m_{AV} and d_{1AV} for FOX-7 are included in this appendix. The Molecular weight, MW, is also calculated.

Computation of m_{AV} for FOX-7

Table A-1. Mass of a Single Atom for Selected Elements

Element	AW Grams Gram - Mole	N_{AV} Atoms Gram - Mole	m Grams Atom
Carbon (C)	12.011	$6.02252(10^{23})$	$1.9943(10^{-23})$
Hydrogen (H)	1.008	$6.02252(10^{23})$	$0.1674(10^{-23})$
Nitrogen (N)	14.008	$6.02252(10^{23})$	$2.3259(10^{-23})$
Oxygen (O)	16.00	$6.02252(10^{23})$	$2.6567(10^{-23})$

FOX-7 chemical composition: $C_2 H_4 N_4 O_4$ [8, 11]

Table A-2. FOX-7 m_{AV} Computation

C_2 2 x 1.9943 (10^{-23}) = 3.9886 (10^{-23}) Grams
H_4 4 x 0.1674 (10^{-23}) = 0.6696 (10^{-23}) Grams
N_4 4 x 2.3259 (10^{-23}) = 9.3036 (10^{-23}) Grams
O_4 4 x 2.6567 (10^{-23}) = 10.6268 (10^{-23}) Grams
14 Atoms weigh 24.5886 (10^{-23}) Grams

$$m_{AV} = \frac{24.5886\,(10^{-23})\ \text{Grams}}{14\ \text{Atoms}} = 1.756329\,(10^{-23})\ \frac{\text{Grams}}{\text{Atoms}}$$

$$\approx 1.7563\,(10^{-23})\ \text{Grams per average Atom}$$

Computation of d_{1AV} for FOX-7

Reference [11] gives the following density values for FOX-7.

$\rho_\circ$ = 1.65 Grams/CC (for small scale gap test)

$\rho_\circ$ = 1.878 Grams/CC (for crystal density)

For $\rho_\circ$ = 1.65 Grams/CC

$$d_{1AV}{}^3 = \frac{m_{AV}}{\rho_\circ} = \frac{17.563\,(10^{-24})}{1.65}\ \frac{\text{Grams}}{\text{Grams/CC}} = \text{CM}^3$$

$$= 10.644242\ (10^{-24})\ \text{CM}^3$$

$$d_{1AV} = 2.199741\ (10^{-8})\ \text{CM} = 2.1997\ \text{Å}$$

For $\rho_\circ$ = 1.878 Grams/CC

$$d_{1AV}{}^3 = \frac{m_{AV}}{\rho_\circ} = \frac{17.563\,(10^{-24})}{1.878}\ \frac{\text{Grams}}{\text{Grams/CC}} = \text{CM}^3$$

$$= 9.351970\ (10^{-24})\ \text{CM}^3$$

$$d_{1AV} = 2.106852\ (10^{-8})\ \text{CM} = 2.1069\ \text{Å}$$

These values for d_{1AV} are much larger than C(1) – C(2) bond lengths (1.456 Å) and N(12) – O(22) bond lengths (1.242 Å) given in Reference [11]. However, Figure 6 of Reference [11] shows a layered structure of the molecules where the minimum separation distance between nitrogen and oxygen atoms is 3.11 Å. So the average distance between atoms is approximately 2.10 Å as shown in the above computations.

Computation of MW for FOX-7

Chemical formula = $C_2 H_4 N_4 O_4$ = $C_i H_j N_k O_l$

Table A-3. MW Calculation for $C_2 H_4 N_4 O_4$

Element	AW $\frac{\text{grams}}{\text{gram - mole}}$	n $\sim$	n x AW $\frac{\text{grams}}{\text{gram - mole}}$	
Carbon (C)	12.011	i = 2	24.022	Grams
Hydrogen (H)	1.008	j = 4	4.032	Grams
Nitrogen (N)	14.008	k = 4	56.032	Grams
Oxygen (O)	16.000	l = 4	64.000	Grams
MW = $\sum$ n x AW		=	148.086	$\frac{\text{grams}}{\text{mole}}$

So MW = 148.086 Grams $\approx$ 148 Grams

NAPMW = $\frac{MW}{m_{AV}}$ = $\frac{148.086}{1.756329(10^{-23})} \frac{\text{Grams}}{\left(\frac{\text{Grams}}{\text{Atom}}\right)}$ = Atoms

= $84.315638\ 10^{+23}$ Atoms per mole

This checks well with:

NAPMW = $q\ N_{AV}$ = $(14.0)\ (6.02252 * 10^{+23})$

= $84.315280 * 10^{+23}$

Where: $q = \sum n = i + j + k + l = 2 + 4 + 4 + 4 = 14 \frac{\text{Atoms}}{\text{Molecule}}$

N_{AV} = Avogadro's number – No. of molecules per MW. (Molecules/MW)

APPENDIX B
SPECIFIC HEAT (C_P) UNITS CONVERSION RELATIONS

Appendix B

Specific Heat (C_P) Conversion Relations

Experimental Specific heat data are usually given in calories (cal) or Joules (J) per molecular weight (MW) per ° centigrade (°C) or ° Kelvin (°K). That is:

$C_P = C_P$ (cal. per MW per ° C or °K)

or

$C_P = C_P$ (J per MW per °C or °K).

Occasionally, C_P is presented as cal. or J per gram °C or °K.

$C_P = C_P$ (cal per gram per °C or °K)

or

Cp = Cp (J per gram per °C or °K)

Note that:

Cp (cal. or J per gram per °C of °K) = Cp (cal, or J per MW per °C or °K)/MW.

Since interest is in Cp (cal or J per atom per °C or °K) then, Cp (cal. or J per atom per °C or °K = m_{AV} Cp (cal. or J per gram per °C or °K).

See Appendix A for procedures to determine m_{AV}. Note that 1° C = 1° K, and that the conversion factor between Joules and calories is 4.184 so that:

Cp (J per atom per °K) = 4.184 * Cp (cal per atom per °K).

Also, since 1 Joule = 10^7 ergs = 10^7 grams $(cm/sec)^2$

then,

Cp grams $(cm^2/sec^{2)}$ per atom per °K = 10^7. (J per atom per °K).

The above relations were employed in Reference 2, and the present report. However, Cp can also be given in terms of a velocity squared per °K as follows:

Cp$(cm^2/sec^2$ per °K) = 10^7 x Cp (J per gram per °K). In these units for Cp, $\Delta(v.e.)_{TR} = \int_{T_{EXP}}^{T_R} C_p dT = (cm/sec)^2$, so $U_{PCR1} = \sqrt{\Delta(v.e.)_{TR}}$ = and $U_{PCR2} = \sqrt{2\Delta(v.e)_{TR}} = \sqrt{2}\ U_{PCR1}$.

This eliminates having to compute an average mass (m_{AV}) and the C_P in calories or Joules per average atom.

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